

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : TOYOTA MOTOR CORP

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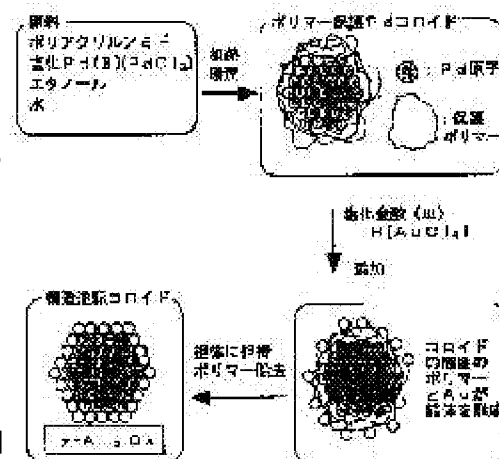
(72)Inventor : HIRATA HIROTO

## (54) COMPOSITE METAL COLLOID AND ITS PRODUCTION AS WELL AS CATALYST FOR PURIFICATION OF GAS AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide composite metal colloid which is controllable in metal species constituting core parts and shell parts regardless oxidation reduction potential and has a reverse structure which is heretofore difficult with the conventional process for production.

SOLUTION: The polymer protective metal colloid consisting of a first metal coated with a protective polymer is prepared and a colloid complex composite obtained by coordinating second metal ions with the protective polymer of the polymer protective metal colloid is formed and thereafter the protective polymer is removed from the colloid complex composite. The core parts may be formed by the first metal and the shell parts by the second metal.



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**CLAIMS**

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[Claim(s)]

[Claim 1]Composite metal colloid becoming a core part which consists of the 1st metal, and a shell part which is formed in the surface of this core part and consists of the 2nd metal whose oxidation-reduction potential is higher than this 1st metal more.

[Claim 2]A process of preparing polymer protection metallic colloid by which the 1st metal was covered by protective polymer, A manufacturing method of composite metal colloid becoming a process of making this protective polymer of this polymer protection metallic colloid configuring the 2nd metal ion, and forming a colloid complex, and the process of removing this protective polymer from this colloid complex, more.

[Claim 3]A catalyst for emission gas purification characterized by comprising the following.  
A carrier which consists of a porosity oxide.

Composite metal colloid which consists of a shell part which is formed in the surface of a core part which consists of the 1st metal supported by this carrier, and this core part, and consists of the 2nd metal whose oxidation-reduction potential is higher than this 1st metal.

[Claim 4]A process of preparing polymer protection metallic colloid by which the 1st metal was covered by protective polymer, A process of making this protective polymer of this polymer protection metallic colloid configuring the 2nd metal ion, and forming a colloid complex, A manufacturing method of a catalyst for emission gas purification becoming a process of supporting this colloid complex to a carrier which consists of a porosity oxide, and the process of removing this protective polymer from this colloid complex, more.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to composite metal colloid, its manufacturing method and the catalyst for emission gas purification using the composite metal colloid, and its manufacturing method.

[0002]

[Description of the Prior Art]As a catalyst for emission gas purification which purifies the exhaust gas of an automobile engine, the catalyst which supported the precious metals, such as platinum (Pt), rhodium (Rh), and palladium (Pd), is widely used for the carrier which consists of porosity oxides, such as alumina (aluminum<sub>2</sub>O<sub>3</sub>). For example, a three way component catalyst supports Pt and Rh to porosity oxides, such as gamma-aluminum<sub>2</sub>O<sub>3</sub>, and it returns and purifies NO<sub>x</sub> in exhaust gas while it oxidizes and purifies HC and CO in exhaust gas. Especially as the precious metals, high Pt of activity is mainly used.

[0003]In order to manufacture catalysts for emission gas purification, such as this three way component catalyst, powdered or the porosity oxide support in the state where the coat was carried out to the honeycomb substrate is contacted in solution, such as a chloride of the precious metals, a nitro complex of the precious metals, and an ammonium complex of the precious metals, and the precious metals are supported with desiccation and calcinating after that in it. The precious metals supported with such a support method are extremely supported by high distribution in the shape of an atom, and the catalyst has very high catalytic activity.

[0004]On the other hand, carbon dioxide (CO<sub>2</sub>) in the exhaust gas discharged from internal-combustion engines, such as a car, is made into a problem from a viewpoint of earth environment protection, and promising \*\* what is called of the lean burn which carries out lean combustion in hyperoxia atmosphere as the solution is carried out in recent years. In this lean burn, in order that fuel consumption may improve, use of fuel is reduced, and generating of CO<sub>2</sub> which is that combustion gas can be controlled.

[0005]On the other hand, the conventional three way component catalyst is what an air-fuel

ratio oxidizes and returns CO in exhaust gas, HC, and NO<sub>x</sub> simultaneously, and purifies in theoretical air fuel ratio (SUTOIKI), Under the hyperoxia atmosphere of the exhaust gas at the time of lean burn, sufficient purification performance is not shown to reduction removal of NO<sub>x</sub>. For this reason, development of the catalyst which can purify NO<sub>x</sub> under hyperoxia atmosphere was desired.

[0006]Then, the applicant for this patent has proposed the catalyst for emission gas purification (for example, JP,5-317625,A) which supported NO<sub>x</sub> occlusion material and Pt(s), such as Ba, to porous carriers, such as alumina, previously. By what (rich spike) an air-fuel ratio is controlled for using this catalyst for emission gas purification to become pulse form from the Lean side SUTOIKI - a rich side. In the Lean side, occlusion of the NO<sub>x</sub> is carried out to NO<sub>x</sub> occlusion material, it is emitted by SUTOIKI - a rich side, and since it reacts to reducible components, such as HC and CO, and is purified, also in lean burn, NO<sub>x</sub> can be purified efficiently.

[0007]In order to manufacture such a NO<sub>x</sub> occlusion reduction type catalyst, the slurry containing a porosity oxide and binders, such as alumina, is prepared, the coat of this slurry is carried out to the honeycomb substrate made from cordierite or a metal, it is calcinated, and a coated layer is formed. And a substrate with a coated layer is immersed in the solution which dissolved the noble metal compound, the precious metals are supported, and NO<sub>x</sub> occlusion material is supported with being immersed in the solution which subsequently dissolved NO<sub>x</sub> occlusion material. A slurry is prepared from NO<sub>x</sub> occlusion material, the carrier powder which supported the precious metals to alumina etc., and a binder, and the manufacturing method which carries out the coat of it to a honeycomb substrate, and calcinates it is also known.

[0008]However, in the conventional three way component catalyst and the NO<sub>x</sub> occlusion reduction type catalyst, although initial use showed high catalytic activity, it had the fault that catalytic activity fell gradually by temporality. This fault appears for the NO<sub>x</sub> occlusion reduction type catalyst which purifies the exhaust gas from a lean burn engine especially notably, pass through it from old research, and the cause of the catalytic activity fall by the time, The precious metals, especially Pt carry out grain growth remarkably in the lean atmosphere of the elevated temperature of hyperoxia during use, and it turns out that it is a thing resulting from a catalytic activity point decreasing due to the fall of surface area.

[0009]In the conventional catalyst, since high distribution support of the Pt is carried out at the shape of an atom, it is thought that grain growth arises with two mechanisms shown below.

(1) At an elevated temperature, in the lean atmosphere of hyperoxia, Pt oxidizes and serves as volatile PtO<sub>2</sub>, and since it is broken away and spread from a carrying position and is caught by other Pt atoms or Pt particles, grain growth produces it.

(2) For example, since Pt and aluminum<sub>2</sub>O<sub>3</sub> have small affinity, Pt atoms or Pt particles tend to move aluminum<sub>2</sub>O<sub>3</sub> carrier surface, repeat a collision and fusion, and grain growth arises.

[0010]Among the above-mentioned mechanisms, in (1), depending on the steam pressure, it breaks away and is easy to diffuse secession and diffusion of  $\text{PtO}_2$  as small particles with big steam pressure, and since it is stabilized by it carrying out grain growth and becoming big particles with small steam pressure, grain growth arises. Therefore, grain growth can be controlled if Pt particles are supported with the particle diameter which breaks away and is hard to diffuse beforehand. On the other hand in the mechanism of (2), grain growth can be controlled by heightening the affinity of Pt and aluminum $_2\text{O}_3$ .

[0011]

[Problem(s) to be Solved by the Invention]Then, using noble metal colloid is recollected and research is advanced. If it is made the composition which supported the precious metals with the state of noble metal colloid, i.e., the composition which supported the precious metals as noble-metal-colloid particles for which the atoms of 10 - a 1000 number gathered, Compared with the conventional catalyst for emission gas purification supported with the shape of an atom, secession and diffusion of  $\text{PtO}_2$  in the lean atmosphere of hyperoxia are controlled at an elevated temperature. Thereby, the grain growth by the mechanism of the above (1) is controlled.

[0012]For example,  $\text{Rh}_2\text{O}_3$  with big carriers, such as aluminum $_2\text{O}_3$ , and affinity,  $\text{RhO}$ ,  $\text{PdO}$ , etc. generate by [ which carry out noble metal composite colloid ] having composite-ized Pt, Rh, or Pt and Pd. The affinity of noble metal composite colloid and aluminum $_2\text{O}_3$  is also large. Therefore, it is controlled that noble metal composite colloid moves in a carrier top, and the grain growth by the mechanism of (2) is controlled.

[0013>About such noble metal colloid, it is Yonezawa. \*\* "Chemicals and industrial" of volume [ 50th ] No. 2 147- 150 (1997) etc. has an indication. According to invention-in-this-application persons' research. It is also clear that the noble metal composite colloid which the 1st metal and the 2nd metal composite-ized can be prepared by adding ethanol to the mixed water solution of the water soluble salt of the 1st precious metals and the water soluble salt of the 2nd metal, and carrying out a heating rotary flow (Japanese Patent Application No. No. 353890 [ nine to ]).

[0014]However, in the manufacturing method of the above-mentioned noble metal composite colloid, only the noble metal composite colloid which consists of a core part of the precious metals with a high oxidation-reduction potential and a shell part of the precious metals with a low oxidation-reduction potential was able to be manufactured from the relation of the oxidation-reduction potential of the 1st precious metals and the 2nd precious metals. Therefore, the degree of option of the metal kind of the noble metal composite colloid obtained was low, since structure had restriction, catalytic activity also had restriction, and there was also fault from a cost aspect.

[0015]This invention is made in view of such a situation, the metal kind which constitutes a core part and a shell part can be controlled regardless of an oxidation-reduction potential, and it aims at enabling it to manufacture easily the composite metal colloid which makes a difficult

inversion structure in the conventional manufacturing method.

[0016]

[Means for Solving the Problem] There is the feature of composite metal colloid of this invention which solves an aforementioned problem in becoming a core part which consists of the 1st metal, and a shell part which is formed in the surface of a core part and consists of the 2nd metal whose oxidation-reduction potential is higher than the 1st metal more. And the feature of a manufacturing method of composite metal colloid of this invention that this composite metal colloid can be manufactured easily, A process of preparing polymer protection metallic colloid by which the 1st metal was covered by protective polymer, It is in becoming a process of making protective polymer of polymer protection metallic colloid configuring the 2nd metal ion, and forming a colloid complex, and the process of removing protective polymer from a colloid complex, more.

[0017] A carrier which the feature of a catalyst for emission gas purification of this invention becomes from a porosity oxide, Composite metal colloid which consists of a shell part which is formed in the surface of a core part which consists of the 1st metal supported by carrier, and a core part, and consists of the 2nd metal whose oxidation-reduction potential is higher than the 1st metal, The feature of a manufacturing method of a catalyst for emission gas purification of this invention that it is in a thing, \*\* and others, and this catalyst for emission gas purification can be manufactured easily, A process of preparing polymer protection metallic colloid by which the 1st metal was covered by protective polymer, It is in becoming a process of making protective polymer of polymer protection metallic colloid configuring the 2nd metal ion, and forming a colloid complex, a process of supporting a colloid complex to a carrier which consists of a porosity oxide, and the process of removing this protective polymer from a colloid complex, more.

[0018]

[Embodiment of the Invention] In the manufacturing method of composite metal colloid of this invention, the polymer protection metallic colloid covered with protective polymer was prepared, the 1st metal made polymer protection metallic colloid configure the 2nd metal ion, and formed the colloid complex, and, finally protective polymer is removed from the colloid complex.

[0019] For example, composite metal colloid of gold (Au) and copper (Cu) is useful as a methanol reforming catalyst etc. The oxidation-reduction potential of Au is abbreviation-0.5V, and the oxidation-reduction potential of Cu is abbreviation-2V. Therefore, if it is going to manufacture this composite metal colloid using the method of using as noble metal composite colloid by reduction from the mixed water solution indicated by Japanese Patent Application No. No. 353890 [ nine to ], Since the oxidation-reduction potential of Cu was very high, it has manufactured only the composite metal colloid in which it is difficult with which to return and to incorporate into colloid, it makes Au a core part, and makes Cu a shell part.

[0020] The height of an oxidation-reduction potential means that an oxidation-reduction potential is so low that an oxidation-reduction potential is so close to zero that [ that is, ] comparison of the size of the absolute value of an oxidation-reduction potential is said, an

oxidation-reduction potential is so high that the absolute value of an oxidation-reduction potential is large and the absolute value of an oxidation-reduction potential is small. It is  $Au < Pd$  when the oxidation-reduction potential of Pd and Au is compared. Therefore, if noble metal composite colloid is manufactured by reduction from a mixed water solution, only the noble metal composite colloid which makes Au a core part and makes Pd a shell part will be obtained.

[0021]However, by using the manufacturing method of this invention, the metal kind of a core part and a shell part can be chosen regardless of an oxidation-reduction potential. Therefore, the composite metal colloid which makes a core part transition metals, such as Cu with high the composite metal colloid which can be manufactured with the manufacturing method indicated by Japanese Patent Application No. No. 353890 [ nine to ] not only being manufactured but oxidation-reduction potential, Fe, and nickel, and makes Au a shell part can also be manufactured. The noble metal composite colloid which makes Pd a core part and makes Au a shell part can also be manufactured. Similarly, from Pt and Pd, the noble metal composite colloid which makes Pt a core part and makes Pd a shell part can be manufactured.

[0022]The ratio of a core part and a shell part can be variously chosen according to the purpose. The 1st metal and the 2nd metal can be chosen regardless of an oxidation-reduction potential. One kind of metal may be sufficient as the 1st metal that constitutes a core part, and two or more sorts of metal can also be used for it. What is necessary is just to consider it as polymer protection metallic colloid using what was used as composite metal colloid by returning in the liquid phase from the mixed solution of each metal salt, when using two or more sorts of metal. The number of the 2nd metal that constitutes a shell part may also be one, and two or more sorts of metal can also be used. What is necessary is just to make polymer protection metallic colloid configurate two or more sorts of 2nd metal ions, when using two or more sorts of metal.

[0023]What is necessary is to mix the solution and the protective polymer solution of the 1st metal salt, and just to heat, in order to prepare polymer protection metallic colloid in the state where the 1st metal was covered with protective polymer. As this protective polymer, although polyacrylamide, polyacrylic acid, polyethyleneimine, polyethylene imidazoline, a polyvinyl pyrrolidone, etc. are illustrated, Especially the thing that has functional groups which are easy to make a coordinate bond with the 2nd metal ion, such as an imino group, a carbonyl group, and a sulfhydryl group, in a side chain is desirable.

[0024]The 2nd metal ion configures in protective polymer, and a colloid complex is formed in polymer protection metallic colloid. It is in the state which the 2nd metal ion configured in the protective polymer which the 1st metal exists in a center and covers the surface of the 1st metal with this colloid complex. Therefore, by removing protective polymer by a next process, the composite metal colloid which makes the 1st metal a core part and makes the 2nd metal a shell part is obtained. The removal of protective polymer can use a thermal decomposition method, a ligand exchange method, hydrolysis, etc.

[0025]And the core part which was obtained by the manufacturing method of this invention and

which consists of the 1st metal, The composite metal colloid which consists of a shell part which is formed on the surface of a core part, and consists of the 2nd metal whose oxidation-reduction potential is higher than the 1st metal is a thing of the structure of the Cu core Au shell which has a shell part which becomes the circumference of Cu and *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. from Au about a core part, for example. Composite metal colloid of this presentation is useful as a methanol reforming catalyst like the structure composite metal of Au core Cu shell. However, since the surface area of Au becomes very high by considering it as the structure of Cu core Au shell, the amount of Au(s) is lessened, catalytic activity equivalent to composite metal colloid of Au core Cu shell can be secured, and it becomes a cheap catalyst.

[0026] Since noble metal composite colloid of the structure of Pt core Pd shell has catalytic activity equivalent to noble metal composite colloid of the structure of Pd core Pt shell and equivalent activity is acquired in the small amount of Pt(s) for example, it can manufacture with the manufacturing method of this invention, it becomes cheap. Composite metal colloid of this invention which chose the kind of the 1st metal and the 2nd metal appropriately can be made into the catalyst for emission gas purification by supporting to porosity oxide support. As porosity oxide support, publicly known things, such as alumina, silica, zirconia, a titania, zeolite, and silica alumina, can be used. The holding amount in particular of composite metal colloid is not restricted, either, but many things can be set up according to a use or the purpose.

[0027] Like what was manufactured in this catalyst for emission gas purification with the manufacturing method indicated by Japanese Patent Application No. No. 353890 [ nine to ], Since it is also controlled that secession and diffusion of  $\text{PtO}_2$  in the lean atmosphere of hyperoxia, etc. are controlled, and composite metal colloid moves in a carrier top, the grain growth of catalyst precious metals is controlled and it is excellent in endurance. And in order to support composite metal colloid to porosity oxide support, it can also support using the manufactured composite metal colloid, but high distribution support may become difficult. Then, it is desirable to support to a carrier the colloid complex which the 2nd metal ion configured in polymer protection metallic colloid, and to remove the aftercare polymer so that it may say this invention. High distribution support is carried out and the composite metal colloid obtained by this shows very high activity to a carrier.

[0028]

[Example] Hereafter, an example explains this invention concretely.

(Example 1) The routing description figure of the manufacturing method of this example is shown in drawing 1. First, 1.00g ( $9.34 \times 10^{-3}$  mol) weighing of the palladium(II) chloride ( $\text{PdCl}_2$ ) is carried out by Pd conversion, water is added, and it is the whole quantity. The solution which was 200 g is prepared.

[0029] On the other hand, it is water to polyacrylamide fluid (it is a 5 time mol ( $4.70 \times 10^{-2}$  mol) by monomer unit conversion). 200 g and 100 g of ethanol are added, and it is considered as a uniform solution. Two kinds of solutions prepared above are mixed, and it stirs at a room



temperature (25 \*\*) for 24 hours. Then, the heating rotary flow of this solution is carried out at 95 \*\* for 4 hours, and a black colloidal solution is obtained. Furthermore, ethanol was removed using the rotary evaporator and it was considered as the polymer protection Pd colloidal solution.

[0030]To this polymer protection Pd colloidal solution, it is Au conversion about a chloroauric acid (III) ( $\text{H AuCl}_4$ ) solution. In addition, it stirs at a room temperature for 24 hours, and let

0.463g (about [ of Pd ] a  $2.35 \times 10^{-3}$  mol, a 1/4 time mol) be a colloid complex solution. After making water distribute gamma-aluminum  $_2\text{O}_3$  powder and adding some above-mentioned colloid complex solutions here, it condenses and hardens by drying, and it is in  $\text{N}_2$  air current. It calcinated at 350 \*\* for 2 hours, and the catalyst which supports noble metal composite colloid to gamma-aluminum  $_2\text{O}_3$  was acquired.

[0031]The structure of noble metal composite colloid on the acquired catalyst, As it was indicated in drawing 2 and 3 as a high-resolution transmission electron microscope (FE-TEM) using an energy dispersive X-ray analyzer (EDX), it checked by conducting very small field analysis of the central region and adjacent spaces of noble metal composite colloid with spatial resolving power of 1 nm. Analysis was conducted about ten noble metal composite colloid, respectively. A result is shown in Table 1.

[0032]While a central region is mainly concerned with Pd, adjacent spaces are mainly concerned with Au, and it is clearer than Table 1 noble metal composite colloid's to make Pd into a core part and to make Au into a shell part.

(Example 2) Instead of the palladium(II) chloride, noble metal composite colloid was manufactured like Example 1 except having used 1.83g ( $9.34 \times 10^{-3}$  mol) of platinum chloride (II) acid ( $\text{H}_2\text{PtCl}_4$ ) by Pt conversion.

[0033]The structure of the obtained noble metal composite colloid is analyzed like Example 1, and a result is shown in Table 1. While a central region is mainly concerned with Pt, adjacent spaces are mainly concerned with Au, and it is clearer than Table 1 noble metal composite colloid's to make Pt into a core part and to make Au into a shell part.

(Example 3) It is Cu conversion about a copper acetate (II) solution instead of a chloroauric acid (III) solution. Noble metal composite colloid was manufactured like Example 1 except having used 0.149g ( $2.35 \times 10^{-3}$  mol).

[0034]The structure of the obtained noble metal composite colloid is analyzed like Example 1, and a result is shown in Table 1. While a central region is mainly concerned with Pd, adjacent spaces are mainly concerned with Cu, and it is clearer than Table 1 noble metal composite colloid's to make Pd into a core part and to make Cu into a shell part.

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[0035]The structure of the obtained noble metal composite colloid is analyzed like Example 1, and a result is shown in Table 1. While a central region is mainly concerned with Pt, adjacent spaces are mainly concerned with Cu, and it is clearer than Table 1 noble metal composite colloid's to make Pt into a core part and to make Cu into a shell part.

[0036]

[Table 1]

		中心領域 (atom%)	周辺領域 (atom%)	構 造
実施例 1	Pd	88.4~92.7	0 ~ 5.9	Pdコア-Auシェル
	Au	7.3~11.6	94.1~ 100	
実施例 2	Pt	86.2~95.1	0 ~ 9.2	Ptコア-Auシェル
	Au	4.9~13.8	90.8~ 100	
実施例 3	Pd	88.8~93.4	0 ~ 7.9	Pdコア-Cuシェル
	Cu	6.6~11.1	92.1~ 100	
実施例 4	Pt	87.9~96.5	0 ~ 8.7	Ptコア-Cuシェル
	Cu	3.5~12.1	91.3~ 100	

[0037]

[Effect of the Invention]That is, according to this invention, the metal kind which constitutes a core part and a shell part can be controlled regardless of an oxidation-reduction potential, and the composite metal colloid which makes a difficult inversion structure can be manufactured easily and certainly by the conventional manufacturing method. And since transition metals, such as Cu whose reduction potential is very high, Fe, and nickel, can also be made into a shell part, the manifestation of new catalytic activity, etc. are expectable.

[0038]According to the catalyst for emission gas purification of this invention, since grain growth, such as Pt, is controlled, the fall of the catalytic activity by temporality is controlled and it excels in endurance extremely.

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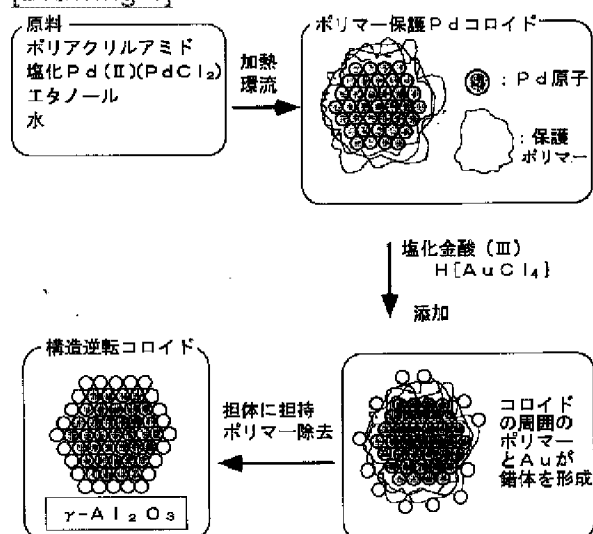
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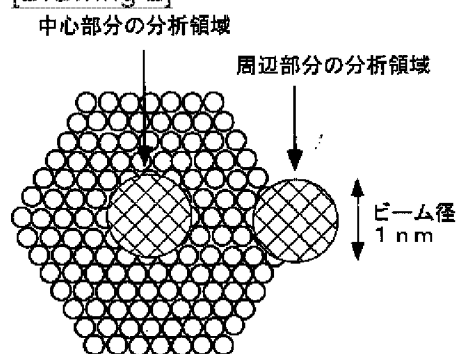
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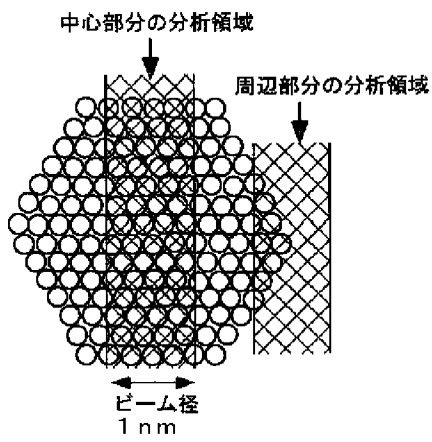
[Drawing 1]



[Drawing 2]



[Drawing 3]



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